

## **REMARKS**

### **Status of the Claims**

Claims 1 and 3-4 are pending in the application.

Claims 1 and 3-4 have been amended to correct grammatical and idiomatic errors. Furthermore, the claims have been amended for clarity. The amendments to the claims do not contain, nor constitute new matter. Support for the amendments to claim 1 can be found in the published application at paragraphs [0034] and [0039].

Claims 2 and 5-8 were previously canceled without prejudice or disclaimer of the subject matter therein.

### **Rejections Under 35 U.S.C § 112**

The Examiner has rejected claims 1, 3 and 4 under U.S.C. § 112, first paragraph, as failing to comply with the written description requirement. It is the Examiner's position that the subject matter of the claims was not disclosed in a way that conveyed that one skilled in the art was in possession of the invention at the time of filing. In particular, the Examiner states that the phrase "metal carbonitride hard coat layer" is not supported by the specification. Applicant notes that claim 1 has been amended to remove this phrase. As such, the Examiner's rejection is now moot, and should be withdrawn.

Claims 1, 3 and 4 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. Specifically it is the Examiner's position that the claims, as drafted, are generally narrative and indefinite, and fail to conform to current U.S. practice. Applicant has amended the claims for clarity and to correct grammatical and idiomatic errors. No new matter was added.

### **Rejections Under 35 U.S.C § 103**

Claims 1 and 3-4 are rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 5,725,932 to Iio et al.

The present invention, as embodied in claim 1, recites a cemented carbide material that is used as a substrate for a surface coated gear cutting tool. This cemented carbide material includes a WC- $\beta$ t-Co based cemented carbide which includes a  $\beta$ t solid solution and a Co element. The  $\beta$ t solid solution is further selected from the following: WC, TiC, TiN and either or both of Ta carbonitride and Nb carbonitride. A critical element of the present invention requires that the Nb content ( $D_{Nb}$ ) and the Ta content ( $D_{Ta}$ ) of the  $\beta$ t solution be provided for in the following ratio  $D_{Nb}/(D_{Nb}+D_{Ta}) \geq 0.7$ . The present invention also discloses that in the carbide the WC and  $\beta$ t elements form a harder phase, while the Co element forms a binder phase. Additionally, claim 1 describes a compact formed of the carbide material that has been sintered in a nitrogen atmosphere and then heat treated at a lower temperature to achieve the final characteristics. The resulting carbide is the product of specific ranges and ratios of the elements combined with specific processing requirements. For example, the content of Co is 12-17 wt%, the WC is in a range of 15 to 20 wt%, and both Ta and Nb are in the range of 5 to 7 wt%. Combining these elements and compounds in specific ratios within given ranges results in a material having superior fracture toughness relative to the cited prior art reference.

In contrast, the cited prior art reference merely discloses a WC based cemented carbide comprising 2-15 wt% Co and/or Ni as a binding phase along with 0.2-20 wt% Ti and Ta and a W-Ti-Ta-C ( $\beta$ t) solid solution. While it is clear that there are overlaps with the ranges disclosed in claim 1, it is obvious that the complete invention as described in claim 1 is not taught by Iio. Furthermore, there is no obvious modification of Iio that teaches the complete invention as described in claim 1.

For instance, it is the Examiner's position that the ratio described by the formula  $D_{Nb}/(D_{Nb}+D_{Ta}) \geq 0.7$  in claim 1 is satisfied by the overlapping disclosures of the prior art. Specifically, the Examiner seeks to demonstrate that the prior art recites that the ratio between the Nb and Ta is between 0 and 1. Iio allows for Ta or Nb to be substituted for one another. However, the critical disclosure of claim 1 is the ratio of Nb to Ta when they are both present. In essence, the formula requires that when both materials are present that Nb be in greater supply than Ta. Nowhere in the prior art is this preferred relationship explicitly taught or suggested. Additionally, the ratio of Nb to Ta, as well as their absolute values by wt%, are disclosed in claim 1. The present

specification makes it clear that the beneficial results are not achieved unless both the content and the ratio of claim 1 are achieved. [0044] to [0049]

Iio merely describes that the amount of Ta can be substituted “in whole or in part” by Nb. This does not describe the relationship that Nb and Tb must share if they are both present in the composition, while also maintaining the proper ratio. Iio fails to describe this relationship, or provide any suggestion or motivation for why the relationship is preferable to merely “substituting” Ta for Nb.

Additionally, the cited reference is silent as to the nature of the processing environment. The product described in claim 1 is processed in an N<sub>2</sub> atmosphere. Iio is largely silent as to the conditions regarding processing. The sole processing information available in Iio is derived from the examples. The examples suggest that the processing conditions included either a vacuum or an inert gas atmosphere. In fact, Iio teaches away from the use of N gas. Iio discloses that in the situations where an N-containing cemented carbide is obtained by sintering in an atmosphere containing nitrogen atoms, it is difficult to produce a surface layer that does not peel off, and hence lacks structural integrity. Furthermore, Iio teaches that it becomes difficult or impossible to control the state of the surface irregularities by controlling the atmosphere in heat treatment of the steps described by Iio. Column 8, lines 1-20 and 54- 63 of Iio.

Therefore, one skilled in the art would not be motivated to conduct the sintering of the material powders in a nitrogen atmosphere as described in amended claim 1. As such, the cited prior art reference fails to teach the complete invention of claim 1.

Furthermore, claim 1 provides a product that is heat treated at a temperature (500 °C) that is significantly lower than its sintering temperature (1400 °C), while under a standard atmospheric pressure. [0039] [0034] In contrast, the prior art recites a WC-based cemented carbide material sintered at a temperature (1400-1500°C) that is slightly higher than the temperature used for heat treatment (1350-1450 °C). See Column 9, lines 3-6, 11, lines 1-4 and Column 12, lines 34-39. Therefore, the prior art teaches away from one of the critical elements of claim 1. Furthermore, there is no motivation or suggestion to alter the prior art to provide for a temperature that is higher than the sintering temperature of the WC-base cemented carbide.

Lastly, the product produced by the prior art reference is believed to be inferior to the present invention because it lacks an even distribution of the  $\beta(N)$  phase on the surface layer of the cemented carbide piece. The N-containing surface layer presents irregularities due to both the formulation of the WC-carbide piece, as well as the temperatures at which the material is formed. Evidence of the incomplete and uneven distribution can be seen in Fig 12, of Iio. Furthermore, Tables 2, 3, and 5 further confirm the uneven nature of the  $\beta(N)$  phase distribution. See column titled "Modified Surface layer presence or not of modified surface layer formed of  $\beta(N)$  phase".

Applicant provides further support for the failure of the prior art to replicate the characteristics of the product described in the present invention in the form of the attached NPL document Hisashi Suzuki, "Cemented Carbide And Sintered Hard Material," 1986, pp.302 -303, (English language abstract attached and herein referenced as "Suzuki reference"). To the best of Applicant's knowledge, the English Abstract is an accurate translation and summary of the subject matter contained within the NPL document. The Suzuki reference provides an analysis of a low carbon, a low-carbon alloy of WC-33.3%;  $\beta$ -12.1%; and Co that is sintered at 1400°C in a vacuum, and then heat treated at 1250°C in N<sub>2</sub> atmosphere having a pressure of 0.9 atm for either one of 3 hours, 6 hours, or 12 hours. See FIG. 1.396 (page 303). This process and conditions are significantly similar to those described in Iio, with the exception of N<sub>2</sub> atmospheric processing. Figure 1.396 clearly shows the resulting microstructure of a cross-section of the alloy. This figure is also reproduced in the English abstract. The results of the process described are a hard layer formed only in the surface, and the inner of the alloy lacking sufficient nitride characteristics.

Therefore, from the center to the surface of the WC-based cemented carbide piece of Iio fails to possess the specific characteristics of the present invention. In particular, since the  $\beta(N)$  phase is unevenly distributed in the surface, the  $\beta(N)$  phase does not sufficiently penetrate the inner portion of the WC-based cemented carbide piece. Therefore, the enhanced structural strength of the  $\beta(N)$  phase cannot be obtained in all portions the WC-based cemented carbide piece. As a result superior fracture toughness throughout the material is impossible.

In light of the teaching from Suzuki, even if it were obvious to modify the atmosphere of the prior art with the teaching of the Suzuki reference, the combined teaching still fails to achieve the invention as described in claim 1. Additionally, The Examiner has provided no suggestion or

motivation as to how Iio would be obviously modified so as to provide the improved characteristics found in the present invention relating to the various ratios, ranges and processing elements. In fact, the prior art is clearly inferior, and that inferiority is the result of both the differences in processing, as well as the failure to achieve the provided ratio between Nb and Ta as described in amended claim 1.

Accordingly, the cemented carbide material of the present invention is not obvious in light of Iio. In light of the foregoing arguments and amendments, the rejection under 35 U.S.C. §103(a) are now moot and should be removed. Applicant also notes that claims 3-4 are dependent directly from claim 1. As such, the foregoing arguments render them likewise non-obvious in light of the cited prior art. As such, the 35 U.S.C. § 103(a) rejection that applies to the dependent claims should likewise be removed.

**CONCLUSION**

In view of the foregoing arguments and claim amendments, each of the presently pending claims in this application is believed to be in immediate condition for allowance. Accordingly, the Examiner is respectfully requested to pass this application to issue.

The Examiner is respectfully requested to contact the undersigned at the telephone number indicated below if the Examiner believes any issue can be resolved through either a Supplemental Response or an Examiner's Amendment. In view of the above amendment, Applicant believes the pending application is in condition for allowance.

The Commissioner is hereby authorized to charge any unpaid fees deemed required in connection with this submission, or to credit any overpayment, to Deposit Account No. 50-4570.

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Respectfully submitted,



By \_\_\_\_\_  
Jordan Garner  
Registration No.: 60,148  
LEASON ELLIS LLP.  
One Barker Avenue  
Fifth Floor  
White Plains, New York 10601  
(914) 288-0022  
(914) 288-0023 (Fax)  
Attorneys for Applicants

はここで略すが、要するに N 量が多ければ相域が低炭素側へずれるのは当然であり ( $\beta(N)$  中の C+N の合計量は一定),  $a_{\beta(N)}$  の格子定数が低くなるのは, N のほうが C よりも原子径が小さいためである。保持時間が長くなるほど,  $a_{\beta(N)}$  が大きくなるのは, 焼結中に  $\beta(N)$  中へ浸炭がなされるためである。図 1.388<sup>92)</sup> には  $\beta(N)$  合金の抗折力を  $\beta$  合金と比較して示した。図には普通焼結合金 (NS 状態) と HIP 合金 (HIP) の結果を掲げ, それぞれ合金炭素量を変化させている。これによると NS 状態で  $\beta(N)$  合金は  $\beta$  合金よりも低強度であるが, HIP 処理により, 著しく高強度となることが注目される。そして低炭素 (L.C.) の  $\beta(N)$  合金は最も強い。図 1.389<sup>93)</sup> は  $\beta(N)+TaC$  合金に関する結果である。傾向は前と同様であるが, HIP 合金の強さが TaC の添加量によってほとんど変わ

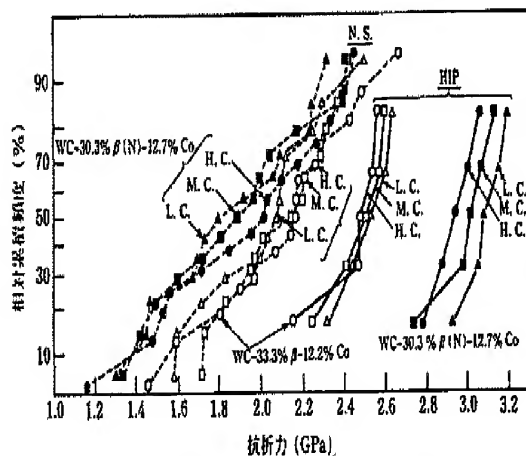


図 1.388  $\beta(N)$  合金と  $\beta$  合金の抗折力比較。N.S., 焼結状態; HIP, 焼結後 HIP (鈴木ら)

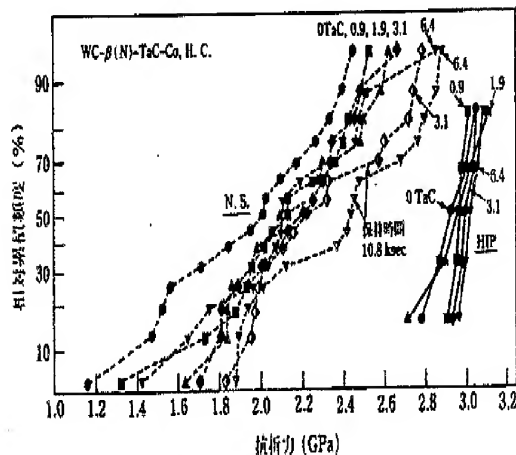


図 1.389 ( $\beta(N)+TaC$ ) 合金の抗折力

らないことが注目される。N を添加した合金の強さが, HIP 状態で, 著しく優れる理由は現在必ずしも明確でないが, この現象は N 添加の第三の利点としてあげることができる。N 添加合金については, 最適な N 添加量, NS 状態でポア発生を防止する方法, 省 Ta 量の限界などが今後の課題となろう。

最後に, N 添加の第四の利点を付記する。これは省 Ta とは関係がないことであるが, WC- $\beta(\beta_1)$ -Co 系合金に少量の N を含ませ, これを脱窒条件下で焼結すると, そのほか焼結雰囲気中の調整などにより, 合金表面に脱  $\beta$  層を生じさせることができるのである。詳細は次項で述べる。

### 1.7.7 表面に変質層を有する超硬合金

#### a. 脱 $\beta$ 層を有する超硬合金

WC- $\beta$ -Co あるいは WC- $\beta_1$ -Co 合金中にあらかじめ窒素 (N) を添加しておき, これを脱窒雰囲気中で焼結すると試料表面

に  $\beta$  や  $\beta_1$  相が消失した層 (脱  $\beta$  層)

が生じる<sup>94)~100)</sup>。この場合 N 添加法

には, 混合粉中に TiN, TaN などの

窒化物を加える方法; N を含む

$\beta_1, \beta_2$  (それぞれ  $\beta(N), \beta_1(N)$ ) を用

いる方法; 混合粉中には N を添加

しないが, 焼結雰囲気中に少量の

$N_2$  ガスを導入し, 低温で加窒させ

て, 焼結中に脱窒させる方法などが

ある。この機構については後述する

が, このほか, N とは無関係に,

焼結後に雰囲気中を脱窒雰囲気に切り

換えて, 保持または徐冷却しても,

脱  $\beta$  層 (または  $\beta$  相濃度を減少させ

た層) をうることができる。脱  $\beta$

層の組織例を図 1.390<sup>100)</sup> に示した。

図 1.391 には表面部の  $\beta$  相濃度を

低下 (Co 濃度は上昇) させた母材上

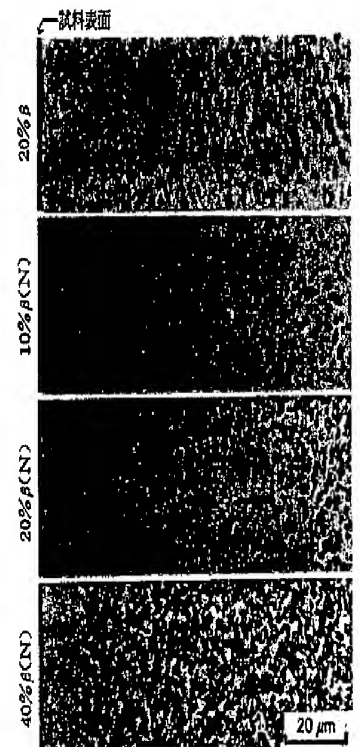


図 1.390 WC-20%  $\beta$ -Co および WC-(10~40)%  $\beta(N)$ -Co 合金の試料表面組織。いずれも高炭素合金。Co の体積率は 16.4%。 $\beta(N)$  は 70/30  $\beta$  中に約 4% N を含ませたもの (Suzuki ら)

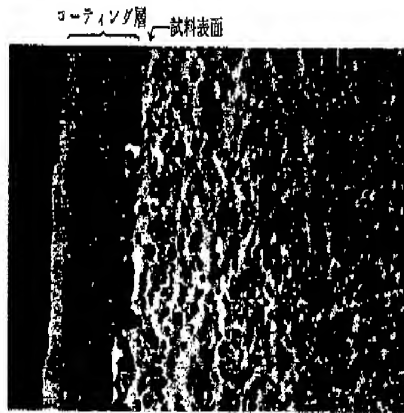


図 1.391 表面部の  $\beta$  相濃度を低下させた母材上に、TiC/Ti(C,N)/TiN の三層コートをしたときの断面組織。×1000 (ダイジェット工業, KC 850)

に、TiC/Ti(C,N)/TiN の三層コートを行ったときの断面組織である。これより、試料表面部は WC-Co 合金になったり、Co が富化されるために内部よりも靱性が高くなる。したがって、脱  $\beta$  層などを有する合金は、CVD 被覆超合金 (1.6.1) の専用母材として、重要な役割を果たしつつあるのが現状である。住友電工のエースコート<sup>TM</sup>は脱  $\beta$  層を利用したものであり、CVD 被覆用には各社ともいふ述べたような専用母材を用いている。

CVD 専用母材として用いる場合、脱  $\beta$  層については、その厚さのコントロールが肝要であるが、1.6.1 a では関連の記述が略されているので、以下これに関する結果<sup>140)</sup>を要約する。図 1.392<sup>140)</sup>は WC-20% $\beta$ (N)-Co 合金 ( $\beta$ (N) は 70/30 $\beta$  中に N が 4% 含有、Co の体積率は 16.4%) に生じる脱  $\beta$  層の厚さ ( $x$ ) に及ぼす合金炭素量、焼結温度、焼

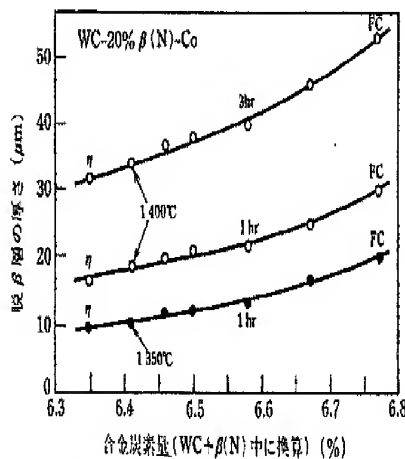


図 1.392 脱  $\beta$  層の厚さに及ぼす合金炭素量、焼結温度、焼結時間の影響。Co の体積率、 $\beta$ (N) 組成は図 1.390 と同じ

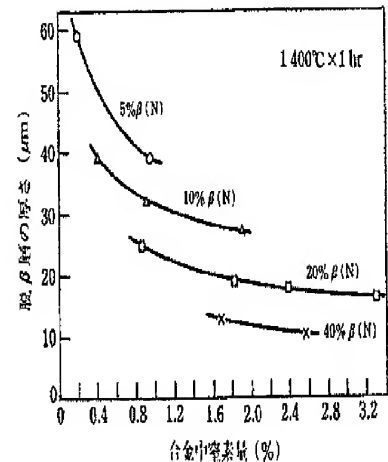


図 1.393 脱  $\beta$  層の厚さと合金中窒素量との関係。高炭素合金。Co の体積率は 16.4%。窒素含有量の異なる  $\beta$ (N) 粉末使用。(Suzuki ら)

結時間の影響を示す。x は高炭素合金ほど、焼結温度が高いほど、焼結時間が長いほど増加する。このとき、焼結時の真空度を高めると、x はさらに増加する。図 1.393<sup>140)</sup>は x と合金中 N 量との関係である。ここで各試料の  $\beta$ (N) 量は 5~40% と変化しているが、 $\beta$ (N) 量が同一の合金については、 $\beta$ (N) 中の N 含有量を変化させることにより、合金中の N 量を変えている。これより、合金中の N 量が増加すると x は減少し、N 量が同一の合金であっても  $\beta$ (N) 量が多くな

るほど x は減少する。図 1.394<sup>140)</sup>は WC-(5~40)% $\beta$ (N)-Co 合金 ( $\beta$ (N) 中の N 量、4%) において x に及ぼす焼結時間 ( $t$ ) の影響を調べた結果である。明らかに  $x \propto \sqrt{t}$  の関係が成立する。x と Co 体積率との間にも同様な関係が成立するという。この結果は脱  $\beta$  相の厚さ増加速度が、焼結時液相を通して N が試料外に拡散・放出される過程によって律せられることを示す。N が試料外に放出されると、試料表面部では N 濃度が減少するが、これに

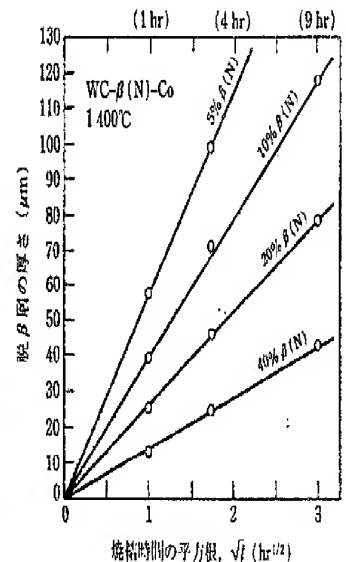


図 1.394 脱  $\beta$  層の厚さに及ぼす焼結時間の影響。高炭素合金。Co の体積率は 16.4%



よって合金は一種の低炭素状態になる。そうすると表面部では  $\beta(N)$  が溶解し、液相中の W, Ti などの溶質濃度が試料内部よりも増加する。すなわち、表面部から内部に向かって溶質が拡散し、脱  $\beta$  層が形成される。試料断面における W, Ti, Co の濃度分布を図 1.395<sup>(10)</sup> に示した。脱  $\beta$  層内では Co 濃度が高くなり、脱  $\beta$  層の内側では Ti が濃縮されていることが分る。ここで詳細は略すが、脱  $\beta$  層の厚さ ( $x$ ) と諸要因との関係は、焼結温度を一定とすると、次式で示されるという。

$$x = \left( \frac{2af_T \cdot D_N \cdot ([N]_b - [N]_i) \cdot t}{C_N} \right)^{1/2} \quad (1.45)$$

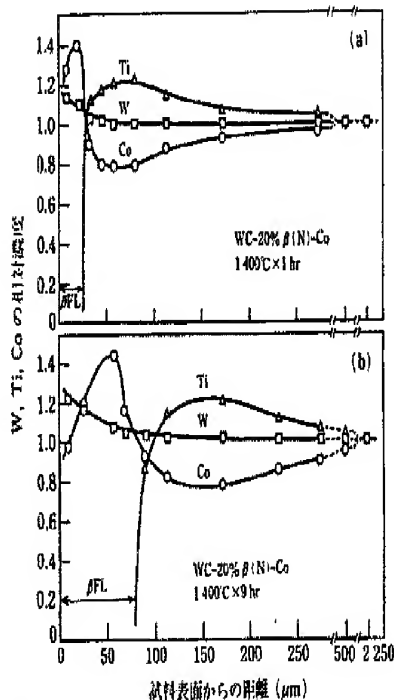


図 1.395 脱  $\beta$  層を生じた試料断面における W, Ti, Co の濃度分布 (EPMA 分析による)。高炭素合金。Co の体積率は 16.4%。βFL, 脱  $\beta$  層。(Suzuki ら)

式中の記号は次のとおりである。  $f_T$ , 固相状態での  $\gamma$  相 (Co 相) の体積率;  $af_T$ , 脱  $\beta$  層内における液相の体積率;  $D_N$ , 液相中での N の拡散係数;  $[N]_b$  と  $[N]_i$ , それぞれ脱  $\beta$  層境界部および試料表面における液相中での N 濃度;  $t$ , 焼結時間;  $C_N$ , 合金中の N 濃度。

#### b. 表面に硬質層を有する超硬合金

上述した a 項の内容から直ちに分るように、低炭素の WC- $\beta$ (N)-Co 合金をまず焼結

し、続いて焼結雰囲気を変化性または浸炭性とする ( $N_2$ ,  $CH_4$  ガスなどの導入) と、表面に今度は硬質相を生じることになる。図 1.396<sup>(12)</sup> は WC-33.3% $\beta$ -12.1%Co ( $\beta$  と Co の体積率はそれぞれ 41.8%, 16.4%) 低炭素合金を 1400°C で真空焼結後、0.9 気圧の  $N_2$  中 1250°C で各時間加熱したときの断面組織例である。表面には確かに硬質層が生じている。CVD, PVD 法による被覆超硬合金が現在広く用いられている (1.6.1; 1.6.2) が、本法は硬質層形成に対して新しい手法を示唆するものである。

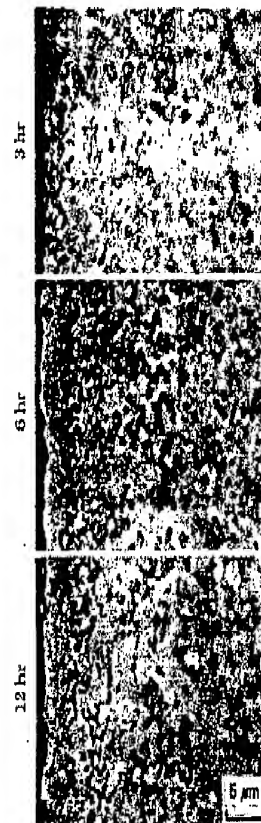


図 1.396 WC-33.3% $\beta$ -12.1%Co 低炭素合金を 1400°C で真空焼結後、0.9 気圧の  $N_2$  気中で各時間保持したときの断面組織。表面に硬質層を生じを示す(林ら)

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## Z

Zener-Holloman の式 184  
 Zn 添加合金 146, 258  
 ZrC 2, 71  
 Zr-C 系状態図 71, 72  
 ZrC 添加サーメット 364  
 Zr-Hf-C 79  
 ZrN 85, 90  
 Zr-N 系状態図 85, 88  
 Zr(O) 分散セラミックス 394  
 Zr(O)-Y<sub>2</sub>O<sub>3</sub> 系状態図 393  
 (Zr, W, Ti)C 固溶体炭化物 332

 $\beta$ 

$\beta$  相 66, 79, 98, 101  
 $\beta$ -MoC-Ni 合金 323, 337  
 $\beta$ (N) 296  
 $\beta$ (N) 焼結体 272  
 $\beta$ -Ni 合金 323, 337  
 $\beta$ <sub>1</sub> 相 66, 98

$\beta$ <sub>1</sub> 相の格子定数 100, 101, 131  
 $\beta$ <sub>1</sub> の組成 101

 $\gamma$ 

$\gamma$ '(NiAl) 292  
 $\gamma$  相 66, 98, 106, 108  
 $\gamma$  相中の炭素の化学ポテンシャル 104  
 $\gamma$  相ドメイン 94, 106, 174  
 $\gamma$  相ドメイン寸法 107  
 $\gamma$  相の格子定数 63, 98, 100, 101  
 $\gamma$  相の格子定数に及ぼす焼なまし時間の影響 108  
 $\gamma$  相の組織 106  
 $\gamma$  相の組成 98  
 $\gamma \rightarrow \delta'$  変態 268, 276

 $\varepsilon, \eta$ 

$\varepsilon$  相 (TiNi) 54, 316  
 $\varepsilon' \rightarrow \gamma$  逆変態 108

$\eta$  相 15, 39, 54, 62, 66, 95, 96, 98, 104

編著者の現職

東京大学工学部教授 工学博士

超硬合金と焼結硬質材料  
 —基礎と応用—

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著者 丸 木 満

発行者 海老原 熊雄

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b. Cemented Carbide Including Hard Layer In Surface

WC- $\beta$ ( $\beta$ t)-Co alloy including a small amount of C is sintered, and then a sintering atmosphere is changed to a nitriding atmosphere or a carburizing atmosphere (gas of N<sub>2</sub>, CH<sub>4</sub> or the like is introduced). As a result, a hard phase is formed in the surface. A low-carbon alloy of WC-33.3% $\beta$ -12.1%Co was sintered at 1400°C in a vacuum, and then a heat treatment was performed at 1250°C in N<sub>2</sub> atmosphere having a pressure of 0.9 atm for either one of 3 hours, 6 hours, or 12 hours. FIG. 1.396 shows a microstructure of a cross-section of the obtained alloy. It can be identified that a hard layer is formed in the surface.

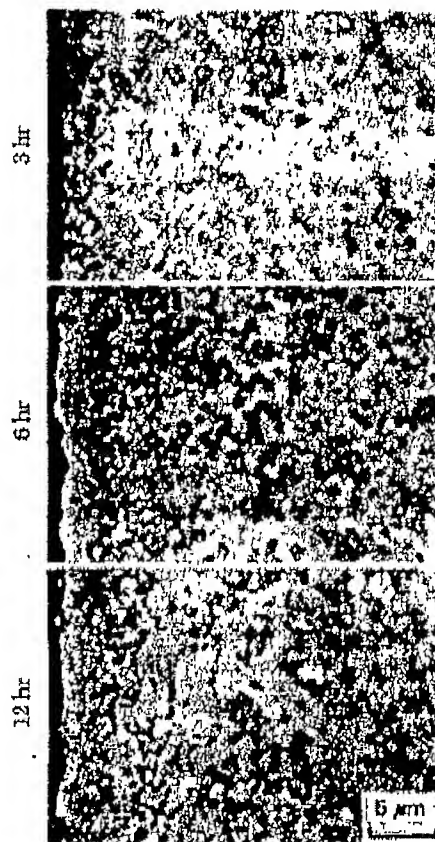


FIG. 1.396 shows a microstructure of a cross-section of an alloy which is obtained by sintering a low-carbon alloy of WC-33.3% $\beta$ -12.1%Co at 1400°C in a vacuum, and then performing a heat treatment at 1250°C in N<sub>2</sub> atmosphere having a pressure of 0.9 atm for each holding time.